Reactions of methyl groups on a non-reducible metal oxide: the reaction
of iodomethane on stoichiometric α -Cr₂O₃(0001)

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ABSTRACT

The reaction of iodomethane on the nearly-stoichiometric α -Cr₂O₃(0001) surface produces gas phase ethylene, methane, and surface iodine adatoms. The reaction is initiated by the dissociation of iodomethane into surface methyl fragments, $-\text{CH}_3$, and iodine adatoms. Methyl fragments bound at surface Cr cation sites undergo a rate-limiting dehydrogenation reaction to methylene, $=\text{CH}_2$. The methylene intermediates formed from methyl dehydrogenation can undergo coupling reactions to produce ethylene via two principle reaction pathways: (1) direct coupling of methylene and (2) methylene insertion into the methyl surface bond to form surface ethyl groups which undergo β -H elimination to produce ethylene. The liberated hydrogen also combines with methyl groups to form methane. Iodine adatoms from the dissociation of iodomethane deactivate the surface by simple site blocking of the surface Cr³⁺ cations.

1. Introduction

Methyl is a common intermediate encountered in the catalysis of hydrocarbons, and has been shown to be an active species in the partial oxidation of methane [1] and the coupling of methane into higher hydrocarbons [2,3]. Ultra-high vacuum studies of methyl intermediates on metal surfaces show that the most common reaction pathways of methyl are hydrogenation to produce methane and decomposition to surface carbon [4]. C-C bond formation to produce ethane is seen on silver and gold surfaces [5-7], while ethylene is produced on copper surfaces by methylene ($=CH_2$) formed from the dehydrogenation of methyl. Two routes to ethylene production have been observed: (1) direct coupling of two methylenes, and (2) the migration and insertion of methylene into methyl, with β -H elimination of the resulting ethyl species [8-10].

Henderson has examined the thermal and photochemical interaction of methyl bromide with α -Cr₂O₃(0001) [11]. CH₃Br is thermally unreactive on most surfaces [11], and adsorbs and desorbs molecularly with no thermal decomposition on α -Cr₂O₃(0001). Irradiation with a Hg arc lamp causes photodesorption and photodecomposition of methyl bromide. Photodecomposition leads to CH₃ group ejection with little or no retention on the surface. Similarly, studies of methyl on well-defined, Fe₃O₄(111) shows methyl radical ejection at all coverages, but also coupling to ethane at high coverages [12].

A few studies of methyl reactions on oxygen-covered metal surfaces have also been done. Studies by Bol *et al.* show that methyl radicals form methoxy and desorb as gas-phase methyl radicals from O-covered Mo(110) [13], while methyls directly add to surface oxygen [14], producing CO₂, CO and formaldehyde on the O-covered Rh(111) surface [15]. Kim *et al.* observed a migratory insertion route for higher alkene production by methylene formed by the dehydrogenation of methyls on Mo(100) with near monolayer coverages of atomic oxygen in 4-

fold hollow sites, but also saw this reaction route suppressed at higher oxygen coverages leading to terminal (Mo=O) surface species [16]. A related HREELS study shows that methyl binds to surface Mo sites[17].

In this study, the dehydrogenation of methyl fragments and migration of the resulting methylene have been observed on a non-reducible, well-defined metal-oxide surface, α -Cr₂O₃(0001). Methyl intermediates have been generated through the thermal dissociation of iodomethane (CH₃I) and studied experimentally with temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). First-principles DFT calculations have been used to examine the methyl adsorption on α -Cr₂O₃(0001).

2. α -Cr₂O₃

α -Cr₂O₃ has a corundum bulk structure, and is an insulator with a band gap of 3.2 eV [18-21]. Cr³⁺ cations in the bulk are surrounded with six O²⁻ anions in distorted octahedra, while each anion is surrounded with a tetrahedron of four metal cations. Among the possible cation sites, one-third of the sites are vacant along the $[10\bar{1}2]$ direction [22]. Along the [0001] direction, three atomic planes provide a stoichiometric repeating unit with compositions of [Cr, 3O, Cr]. Cleavage between the planes of closely-lying Cr layers yields a hexagonal, non-polar, stoichiometric α -Cr₂O₃(0001) surface (Figure 1). The resulting surface exposes 3-fold coordinated cations (three coordination vacancies) and 3-fold coordinated anions (one coordination vacancy). On the ideal unrelaxed surface, the cations are separated by 4.9 Å, effectively isolating the metal reaction centers.

3. Methods

3.1. Experimental Methods

Reaction experiments were conducted in an ion-pumped, ultra-high vacuum chamber with a base operating pressure of 1×10^{-10} Torr. The chamber was equipped with a Physical Electronics model 15-555 single-pass CMA for Auger electron spectroscopy (AES), an Inficon Quadrex 200 mass spectrometer for temperature programmed desorption (TPD) experiments, and a Princeton Research Instruments model RVL 8-120 reverse view low-energy electron diffraction (LEED) optics.

Soft X-ray photoelectron spectroscopy (XPS) was performed in a separate vacuum system at the U12a beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. All photoemission spectra were collected at an instrumental resolution of 0.5 eV using 350 eV photons. The spectra are referenced to a Cr $2p_{3/2}$ binding energy of 576.9 eV [23]. For the data taken at $h\nu = 350$ eV, the Cr 3p photoemission feature was used as an internal reference and compared to the Cr $2p_{3/2}$ feature in separate runs using $h\nu = 700$ eV. Compensation for surface charging during XPS was achieved with a Gammapdata Scienta FG-300 flood gun using 0.5 eV electrons. The base operating pressure for this system was 1×10^{-10} Torr.

The α -Cr₂O₃ crystal was oriented to within 1° of the (0001) surface using Laue back-reflection and polished to a final mirror finish with 0.25 μ m diamond paste. The sample was mechanically clamped onto a tantalum stage that was fastened to LN₂-cooled copper conductors. Direct sample temperature measurement was achieved with a type K thermocouple attached to the back of the single crystal through a hole in the stage using Aremco No. 569 ceramic cement.

α -Cr₂O₃(0001) surfaces described in the literature have been prepared by the direct oxidation of Cr(110) with 10 to 20 L of oxygen at 625 K followed by annealing in vacuum at 925 K [24] and by molecular beam epitaxy on α -Al₂O₃ substrates [25]. For the epitaxial thin films, Henderson and Chambers [25] were able to prepare stoichiometric surfaces by 500 eV Ar⁺

ion bombardment and annealing at 850 K. Using adsorbed water as a probe, they demonstrated that dissociative and molecular adsorption of H₂O occurs on terrace sites [25,26], and gives a characteristic fingerprint for water desorption from the stoichiometric surface.

The studies reported here were conducted on a (0001)-terminated bulk single crystal of α -Cr₂O₃. We use a simple procedure involving 2 keV ion bombardment and annealing at 900 K in vacuum to clean and order the surface. This treatment produces water desorption traces characteristic of a stoichiometric surface [25], with an additional (small) signal at higher temperatures for trace hydrogen desorption corresponding to the reoxidation of reduced sites by water. The hydrogen generated is attributable to less than 1 % of the total surface Cr site density [27]. This preparation method (2 keV ion bombardment and annealing at 900 K in vacuum) has been utilized because of its simplicity, and because a lower background pressure is realized in the vacuum chamber in the absence of an oxidation step in the preparation procedure. Following sample cleaning and ordering, AES is used to check for surface cleanliness, and LEED is used to confirm the hexagonal (1x1) periodicity characteristic of a simple termination of the bulk material. AES spectra were collected at a primary beam energy of 5 keV. To avoid sample charging due to impinging electron beams, AES was done at 850 K, and LEED was done at 600 K.

Sigma-Aldrich iodomethane (CH₃I) 99.5 %, iodomethane-d₃ (CD₃I) 99.5 atom% D, Sigma-Aldrich dichloromethane (CH₂Cl₂), anhydrous $\geq$ 99.8 %, and Matheson CP grade 99.7 % deuterium (D₂) were used as received. Gas dosing was accomplished by backfilling the chamber through a variable leak valve. The mass spectrometer used for TPD is fitted with a quartz skimmer to enhance the signal from the sample surface, and cover the ionizer to minimize sampling from non-sample surfaces in TPD. [Additionally, TPD runs to specifically sample](#)

desorption from the sample holder were made for comparison to ensure that the reported desorption traces originate from the sample surface. The reported dose sizes have been corrected for ion gauge sensitivity, and all desorption traces and quantities have been corrected for mass spectrometer sensitivity.¹ For TPD, all doses were made at a sample temperature of 90 K, and linear heating ramps were run at 2.5 K/s up to a sample temperature of 830 K. The low heating rate was used to decrease the possibility of thermal fracture of the ceramic sample.

3.2. Computational Methods

All calculations were performed using the projector-augmented-wave method [29,30] within the Vienna Ab-initio Simulation Package (VASP) [31-33]. The Perdue-Burke-Ernzerhof (PBE) approximation was used to treat exchange and correlation utilizing a standard generalized gradient approximation (GGA) [34]. As in our earlier study [35], an 80-atom slab with a vacuum gap of 20 Å was used for all calculations. The 80-atom cell is four stoichiometric [Cr, 3O, Cr] repeat units deep and exposes a (2×2) surface mesh. The atoms in the two lower stoichiometric repeat units were fixed at bulk positions. For all calculations, the initial magnetic moments of the Cr³⁺ cations (d^3) were set following the known antiferromagnetic ordering in α -Cr₂O₃ [36], which is also found to be the ground-state magnetic order using DFT calculations within the GGA [37]. For all geometry optimized structures, the forces on the individual atoms are less than 0.01 eV/Å.

DFT calculations are known to have difficulties in predicting the electronic properties of strongly correlated transition metal oxide materials [37]. It has been suggested that this problem can be overcome with the inclusion of an on-site Coulomb repulsion (DFT+U) [38,39]. A DFT+U study of α -Cr₂O₃ [37] shows that an on-site potential of U=5.0 and J=1.0 leads to an

¹ An ion gauge sensitivity of 9.5 was used for CD₃I using a correlation by S. George as reported by Brainard and Madix (Ref. 28). Relative mass spectrometer sensitivity factors of 0.05 for CD₃I (m/z = 145), 0.23 for CD₂=CD₂ (m/z = 32), and 0.66 for methane (m/z = 20 and 19) were determined experimentally.

acceptable compromise between the structural and electronic properties for the bulk α -Cr₂O₃. In the current study, results for both DFT and DFT+U are presented for comparison. The DFT+U method in the form proposed by Dudarev *et al.* [39] has been used. It is pointed out, however, that the optimal value of the on-site potential for the bulk may not strictly apply to the surface, as mentioned in the study of this surface by Rohrbach et al [37].

4. Results and discussion

The reaction of CD₃I on the nearly-stoichiometric α -Cr₂O₃(0001) surface results in two primary carbon-containing gas phase reaction products and a residual surface product : CD₂=CD₂, CD₄, and surface I adatoms. Multiple m/z signals were monitored simultaneously during the thermal desorption experiments, then compared to the mass spectrometer fragmentation patterns of the suspected product molecules for identification. A m/z signal of 142 was used to track the desorption of the dosed CD₃I molecule, while $m/z = 32, 30, 28$ were used for the identification of CD₂=CD₂, and $m/z = 20$ and 18 for deuterated methane. Contributions of the signal of the dosed reactant molecule (CD₃I) in the product signals were corrected by subtracting the m/z 142 signal from the desorption trace using an intensity based on the mass spectrometer fragmentation pattern of the dosed molecule. Other products were excluded by checking m/z values in the range of 2 to 200. No ethane (CD₃-CD₃), CO, CO₂, or iodized gas phase products other than the dosed molecule were observed. The lack of carbon oxides indicates that the surface is non-reducible under these reaction conditions.

4.1. Thermal Desorption and Reaction of CD₃I

Figure 2 shows the thermal desorption traces following a 0.1 L (1 L = 1×10⁻⁶ Torr·sec) dose of CD₃I on the freshly prepared, nearly stoichiometric surface at 90 K with heating up to 830 K. A small dose size is chosen to minimize the effect of adsorbed iodine on the kinetics and

selectivity of the reactions of methyl, and to also minimize the contribution of fragmentation signals from unreacted methyl iodide in the desorption traces of the product molecules. The desorption signals for the products CD₄, ethylene (CD₂=CD₂) and D₂ occur simultaneously at a peak temperature of 490 K with slight shoulders around 590 K, while the reactant molecule desorbs around 265 K. A low temperature methane feature is seen around 110 K.

Ethylene, D₂, and methane dosed directly on this surface desorb in TPD around 300, 100, and 110 K (not shown), respectively, indicating that the production of these molecules at 490 K from CD₃I is reaction limited. The simultaneous production of CD₂=CD₂, CD₄ and D₂ at 490 K suggests that they originated from a common surface intermediate with the same rate-limiting step. A rate-limiting step that can lead to the production of ethylene and methane from methyl species is the dehydrogenation of methyl: the methyl species dehydrogenate to methylene and surface deuterium atoms (reaction 1). In a separate study of the reaction of methylene species on this surface, the primary reaction for methylene was found to be surface migration and coupling to form ethylene at 480 K [35]. Thus, two methylene moieties formed by the dehydrogenation of methyl species may couple with one another to form ethylene (reaction 2). (An additional route for the production of ethylene from methyl and methylene intermediates is discussed in section 4.2.) Methane (CD₄) is formed by the reaction of liberated deuterium with a remaining methyl group (reaction 3).

In addition to the 0.1 L dose size illustrated in Figure 2, larger doses up to 0.5 L (not shown) were also examined. No variation in the product desorption temperature is seen with

varying coverages, indicating first-order kinetics of the rate-limiting dehydrogenation step. The activation energy barrier for the dehydrogenation of methyl at 490 K determined by the Redhead method [40] for first-order kinetics is 30.9 kcal/mol (1.34 eV) assuming a normal pre-exponential factor of 10^{13} s^{-1} . The methane desorption feature around 110 K is due to the desorption of physisorbed methane formed in the ion pump during the dosing procedure. Ethane ($\text{CD}_3\text{--CD}_3$) is not produced, indicating there is no direct coupling of methyl groups. The lack of ethane production indicates an apparent lack of mobility of surface CH_3 , with the barrier to dehydrogenation lower than a barrier to surface diffusion and coupling. This apparent lack of mobility of surface methyl species would also argue against a concerted CD_3 disproportionation route to the formation of CD_4 and CD_2 .

Figure 3 shows the change of the integrated area for each of the reaction products with consecutive 0.1 L doses. The selectivity among the products from an initially clean surface gives a methane to ethylene ratio ($\text{CD}_4 : \text{CD}_2=\text{CD}_2$) of 1:0.6. Considering the number of carbon atoms in each of these products, it takes the reaction of two methyl intermediates to provide the carbon required to produce a single ethylene molecule (e.g., by methylene coupling), and the hydrogenation of one methyl to produce methane. The (roughly) 2:1 ratio of methane to ethylene therefore suggests that the probability of a methyl group producing either product is similar. The signals of the products CD_4 and $\text{CD}_2=\text{CD}_2$ drop off for later runs due to the site-blocking effect of deposited surface iodine. A similar effect has been seen in our earlier study of the reaction of CH_2Cl_2 on this surface, where the reactivity decreases with increasing Cl coverage, becoming essentially inactive at a Cl/Cr AES ratio corresponding to about one Cl per surface Cr site [41]. We note that iodine could not be quantified with AES in this study due to

the overlap of the signal with the Cr LMM feature from the crystal. However, surface iodine is clearly seen in the XPS experiments described below.

4.2.Methyl and methylene coadsorption study

As mentioned above, methyl intermediates undergo a rate-limiting dehydrogenation reaction to methylene and surface deuterium (reaction 1), leading to the production of CD₄ and CD₂=CD₂. There are, however, two possible pathways to produce ethylene from the dehydrogenation of methyl groups. As seen with the study of methylene species on this surface [35], ethylene can be produced by the migration of methylene intermediates that subsequently couple with one another (reaction 2). Another possibility is that the methylene species migrate and insert into the surface-carbon bond of remaining methyl groups to form a surface ethyl fragment (reaction 4), with these ethyl groups undergoing a subsequent β-D elimination reaction to produce ethylene (reaction 5), as observed on metal surfaces [4].

To test whether the insertion pathway (4 and 5) is operable on this surface, an isotopically labeled coadsorption study has been done. 0.05 L CD₃I was dosed to form -CD₃ methyl fragments, and 0.05 L CH₂Cl₂ to form =CH₂ methylene fragments. Given that C-Cl bond cleavage in CH₂Cl₂ occurs primarily at temperatures below 300 K [35], CH₂=CD₂ production in a temperature range different from that of methyl (-CD₃) dehydrogenation and consistent with the dehydrogenation of ethyl fragments on this surface would indicate the occurrence of the insertion (reaction 6) and β-D elimination pathway (reaction 7).

The result (Figure 4) shows that $\text{CH}_2=\text{CH}_2$ and $\text{CD}_2=\text{CD}_2$ are produced at 465 and 490 K, similar to the temperatures where they are formed from CH_2Cl_2 [35] and CD_3I (this study), respectively. The 465 K reaction channel for $\text{CH}_2=\text{CH}_2$ has been shown to correspond to the direct coupling of methylene to ethylene with surface diffusion as the rate-limiting step [35]. $\text{CH}_2=\text{CD}_2$ is also produced at 465 K (i.e., at the same temperature as $\text{CH}_2=\text{CH}_2$), but at a somewhat lower temperature than the 490 K observed for the maximum rate of dehydrogenation of $-\text{CD}_3$. A peak in $\text{CH}_2=\text{CD}_2$ production at a temperature below the temperature for $-\text{CD}_3$ dehydrogenation indicates an alternative rate-limiting step to methyl dehydrogenation. In addition, a higher-temperature shoulder at 555 K is also observed for $\text{CH}_2=\text{CD}_2$ production that is not seen when methyl groups are the only reactants.

The production of ethylene from ethyl chloride, $\text{CH}_3-\text{CH}_2\text{Cl}$, is also shown in Figure 4 as a grey trace to illustrate the reaction pathways for the dehydrogenation of ethyl species on this surface. Ethyl species are generated by the dissociative adsorption (C–Cl bond cleavage) of $\text{CH}_3-\text{CH}_2\text{Cl}$. Two peaks of ethylene are seen at 395 and 555 K, representing two distinct reaction channels associated with β -H elimination from ethyl on this surface. The origin of the two reaction channels is not well understood, but considering that there is only one reaction channel for β -H elimination and ethylene production from ethyl fragments on the $\text{Cr}_2\text{O}_3(10\bar{1}2)$ surface [42], the multiple pathways are thought to be related to the multiple coordination vacancies available on $\alpha\text{-Cr}_2\text{O}_3(0001)$ cation reaction sites.

The $\text{CH}_2=\text{CD}_2$ peak temperature from the coadsorption of CH_2Cl_2 and CD_3I (465 K) is higher than the low temperature (395 K) pathway for β -H elimination from ethyl groups, but aligns with the diffusion-limited coupling of methylene to $\text{CH}_2=\text{CH}_2$ at 465 K. This result suggests that the migration of methylene to find a methyl fragment is rate-limiting (rather than

the insertion of methylene into the methyl-surface bond), with the subsequent β -H elimination of ethyl to ethylene via a process consistent with the low temperature reaction channel for ethyl dehydrogenation. It is also notable that the shoulder on the high temperature side of the $\text{CH}_2=\text{CD}_2$ desorption trace aligns with the 555 K reaction channel for β -H elimination from ethyl groups.

The results in Figure 4 indicate that the methylene insertion pathway is operable on this surface for the case of coadsorbed methyl and methylene. However, because the primary observation of $\text{CH}_2=\text{CD}_2$ is at temperatures below those associated with methyl dehydrogenation, and since the high-temperature ethyl dehydrogenation channel is not clearly observed for the methyl-iodide-only reaction, the coadsorption experiments do not definitively indicate that insertion is a primary reaction pathway when methyl iodide is the sole reactant.

4.3. X-ray photoelectron spectroscopy

Figure 5 shows the synchrotron-based photoemission results for adsorbed iodomethane. A nearly-stoichiometric surface was dosed with 10 L of iodomethane at 110K, heated to a given temperature, then cooled to near 110 K for the photoemission measurements in an attempt to isolate the surface intermediates formed during the thermally-induced surface reaction of CH_3I . Experiments for C 1s and the I 3d_{5/2} were done in separate runs since different monochromator gratings were required for the selected photon energies.

C 1s XPS spectra using a photon energy of 350 eV are shown in Figure 5(a). The spectrum taken directly after dosing 10 L iodomethane at 110 K shows a single sharp peak at 285.0 eV binding energy. The high binding energy of this feature is attributed to the iodized carbon of molecular CH_3I [5,7,43]. The feature broadens and decreases in intensity upon heating to 200 K to desorb multilayer CH_3I . After heating to 325 K to desorb the remaining molecular

CH₃I adsorbate (as seen in TPD), two contributions are seen as a broadened asymmetric feature extending from about 287 to 282 eV with a maximum at 286.0 eV. Since binding energies near 286 eV are typical of methoxy groups (-O-CH₃) [44], the high binding energy component of this feature suggests that some methyl fragments bind at surface oxygen anion sites following C-I bond breaking of iodomethane. The low BE feature that ranges from 282 to 284 eV is attributed to Cr-bound methyls since typical binding energies for oxygenated carbons are 286 eV or higher [23]. A peak at 284.0 eV remains after heating to 425 K, indicating that surface methyl is mostly Cr-bound prior to the 490 K temperature where the methyl dehydrogenation occurs at a maximum rate. The data suggest that surface Cr cations are the most stable binding sites for methyl fragments. However, it is not clear if dehydrogenation occurs on both cation and anion binding sites, or if methyl groups migrate from anion to adjacent cation sites prior to dehydrogenation. Heating the sample further to 700 K results in the loss of all but a trace amount of carbon over the temperature range associated with product desorption in TPD.

The I 3d_{5/2} spectra using a photon energy of 700 eV are shown in Figure 5(b). A sharp I 3d_{5/2} is observed at a binding energy of 620.9 eV upon dosing at 110 K, characteristic of I in molecular CH₃I [5,7]. This feature decreases in intensity as the sample is heated and the multilayers are removed, while a lower binding energy feature appeared at 619.5 eV. The molecular (higher binding energy) contribution is mostly gone by 330 K, while the lower binding energy feature remains after heating the sample to 700 K. This low binding energy of the remaining I 3d_{5/2} feature is characteristic of a metal iodide [23], and is assigned to I adatoms bound at surface Cr sites, consistent with the apparent site blocking effect of I seen in the TPD experiments.

4.4. DFT calculation results

Geometry optimization of surface methyl on different adsorption sites has been done on the 80-atom unit cell (Figure 6) mentioned previously in the computational methods section. Both DFT and DFT+U predict stable Cr- and O-bound methyl binding configurations in agreement with the XPS results. DFT predicts the Cr-bound methyl (Figure 6(a), Cr-C bond length of 1.99 Å) to be more stable than the O-bound methyl (Figure 6(b), O-C bond length of 1.45 Å) by 1.72 eV. DFT+U predicts the Cr-bound methyl (Figure 6(c), Cr-C bond length of 2.01 Å) to be more stable than the O-bound methyl (Figure 6(d), O-C bond length of 1.45 Å) by only 0.14 eV. Both types of calculations give the proper ordering of the stability of the two binding sites, but with significant differences in energy.

As noted above, the optimal parameterization of the on-site potential for surface cations may not be the same as that determined from bulk properties. However, since we have no quantitative experimental measure of the relative binding strength at the different sites, we have no way to estimate a more appropriate set of parameters for the DFT+U calculation for this adsorption system.

5. Conclusions

The reaction of surface methyl was investigated on the nearly-stoichiometric α -Cr₂O₃(0001) surface via dissociative adsorption of CD₃I. Reaction products seen are methane, ethylene, hydrogen and surface I adatoms. The rate-limiting step for the reaction of surface methyl fragments is the dehydrogenation of methyl groups to methylene. The methylene intermediates formed from the dehydrogenation of methyl migrate across the surface and couple with one another or insert into remaining methyl intermediates to form surface ethyl, which goes through a β -H elimination to produce ethylene as seen in the isotopic labeling results. Surface

hydrogen also combines with methyl groups to form methane. Iodine adatoms from the dissociation of CD_3I deactivate the surface by simple cation site blocking.

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References

- [1] H.F. Liu, R.S. Liu, K.Y. Liew, R.E. Johnson, J.H. Lunsford, *Journal of the American Chemical Society* 106 (1984) 4117.
- [2] H. Schwarz, *Angewandte Chemie International Edition* 50 (2011) 10096.
- [3] R.C. Brady, R. Pettit, *Journal of the American Chemical Society* 102 (1980) 6181.
- [4] B.E. Bent, *Chemical Reviews* 96 (1996) 1361.
- [5] X.L. Zhou, F. Solymosi, P.M. Blass, K.C. Cannon, J.M. White, *Surface Science* 219 (1989) 294.
- [6] X.L. Zhou, J.M. White, *Chemical Physics Letters* 167 (1990) 205.
- [7] X.L. Zhou, J.M. White, *Surface Science* 241 (1991) 270.
- [8] C. Chao-Ming, B.E. Bent, *Surface Science* 279 (1992) 79.
- [9] C.J. Jenks, C.M. Chiang, B.E. Bent, *Journal of the American Chemical Society* 113 (1991) 6308.
- [10] J.L. Lin, C.M. Chiang, C.J. Jenks, M.X. Yang, T.H. Wentzlaff, B.E. Bent, *Journal of Catalysis* 147 (1994) 250.
- [11] M.A. Henderson, *Surface Science* 604 (2010) 1800.
- [12] L. Liu, B.R. Quezada, P.C. Stair, *The Journal of Physical Chemistry C* 114 (2010) 17105.
- [13] K.T. Queeney, D.A. Chen, C.M. Friend, *Journal of the American Chemical Society* 119 (1997) 6945.
- [14] C.W.J. Bol, C.M. Friend, *Journal of the American Chemical Society* 117 (1995) 8053.
- [15] C.W.J. Bol, C.M. Friend, *Surface Science* 337 (1995) L800.
- [16] S.H. Kim, P.C. Stair, *Journal of the American Chemical Society* 120 (1998) 8535.
- [17] B.R. Parker, J.F. Jenkins, P.C. Stair, *Surface Science* 372 (1997) 185.
- [18] R.E. Newnham, Y.M. de Haan, *Zeitschrift für Kristallographie* 117 (1962) 235.
- [19] L. Pauling, S.B. Hendricks, *Journal of the American Chemical Society* 47 (1925) 781.
- [20] D. Adler, in: D.T. Frederick Seitz, E. Henry (Eds.), *Solid State Physics*, 1968, pp. 1.

- [21] J.A. Crawford, Vest, R. W., Journal of Applied Physics 35 (1964) 2413.
- [22] V.E. Henrich, P.A. Cox, The Surface Science of Metal Oxides, Cambridge, Cambridge University Press, 1996.
- [23] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, J. Chastain, Handbook of X-ray Photoelectron Spectroscopy, Perkin–Elmer Corporation, Eden Prairie, MN, 1992.
- [24] J.S. Foord, R.M. Lambert, Surface Science 169 (1986) 327.
- [25] M.A. Henderson, S.A. Chambers, Surface Science 449 (2000) 135.
- [26] V. Maurice, S. Cadot, P. Marcus, Surface Science 471 (2001) 43.
- [27] J.D. Brooks, Model Chromia Surface Chemistry: C₂ Alkyl Fragment Reactions and Probe Molecule Interactions, Blacksburg, VA, Virginia Polytechnic Institute and State University, 2010.
- [28] R.L. Brainard, R.J. Madix, Journal of the American Chemical Society 111 (1989) 3826.
- [29] P.E. Blöchl, Physical Review B 50 (1994) 17953.
- [30] G. Kresse, D. Joubert, Physical Review B 59 (1999) 1758.
- [31] G. Kresse, J. Furthmüller, Physical Review B 54 (1996) 11169.
- [32] G. Kresse, J. Furthmüller, Computational Materials Science 6 (1996) 15.
- [33] G. Kresse, J. Hafner, Physical Review B 47 (1993) 558.
- [34] J.P. Perdew, K. Burke, M. Ernzerhof, Physical Review Letters 77 (1996) 3865.
- [35] Y. Dong, J.D. Brooks, T.-L. Chen, D.R. Mullins, D.F. Cox, Surface Science 632 (2015) 28.
- [36] L.M. Corliss, J.M. Hastings, R. Nathans, G. Shirane, Journal of Applied Physics 36 (1965) 1099.
- [37] A. Rohrbach, J. Hafner, G. Kresse, Physical Review B 70 (2004) 125426.
- [38] V.I. Anisimov, F. Aryasetiawan, A.I. Lichtenstein, Journal of Physics: Condensed Matter 9 (1997) 767.
- [39] S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, A.P. Sutton, Physical Review B 57 (1998) 1505.
- [40] P.A. Redhead, Vacuum 12 (1962) 203.

- [41] Y. Dong, J.D. Brooks, T.-L. Chen, D.R. Mullins, D.F. Cox, Surface Science (In Press).
- [42] J.D. Brooks, Q. Ma, D.F. Cox, Surface Science 603 (2009) 523.
- [43] Z. Francisco, Surface Science 219 (1989) 453.
- [44] R.J. Levis, J. Zhicheng, N. Winograd, Journal of the American Chemical Society 111 (1989) 4605.

FIGURE CAPTIONS

Figure 1. Ball model illustration of the ideal nearly-stoichiometric α -Cr₂O₃ (0001) surface. Small grey spheres represent Cr³⁺ cations and the large red spheres represent the O²⁻ anions.

Figure 2. TPD of 0.1 L CD₃I on the nearly-stoichiometric α -Cr₂O₃(0001).

Figure 3. Integrated signals for each product for consecutive 0.1 L CD₃I TPD runs as a function of cumulative CD₃I exposure.

Figure 4. Ethylene products for 0.05 L CH₂Cl₂ and 0.05 L CD₃I coadsorption TPD. The grey line represents ethylene production from CH₃CH₂Cl TPD.

Figure 5. (a) C 1s and (b) I 3d_{5/2} XPS spectra of Cr₂O₃(0001) dosed with 10 L CH₃I at 110 K and heated to according temperatures.

Figure 6. Configurations of methyl on the α -Cr₂O₃(0001) surface calculated: (a) Cr-bound methyl using DFT, (b) O-bound methyl using DFT (c) Cr-bound methyl using DFT+U, and (d) O-bound methyl using DFT+U. Small blue spheres represent Cr cations, large red spheres O anions, small grey spheres carbon, and the white spheres hydrogen.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

(a)

(b)

(c)

(d)

Figure 6